The ketoses were then isolated as described for psicose. *Maltulose monohydrate* (R_G 0·074) (3·17 g.) crystallised from dioxan–methanol when the solvent was allowed to evaporate slowly at room temperature (Found: C, 40·1; H. 6·7. $C_{12}H_{22}O_{11},H_2O$ requires C, 40·0; H, 6·7%), and had m. p. 113—115° (decomp.), $[\alpha]_D^{20}$ +58° (*c*, 1·58 in H_2O) ⟶ +64° (equilm.). When it was heated with phenylhydrazine acetate solution, maltosazone (m. p. and mixed m. p. 202°) was produced in characteristic crystalline form.

Hydrolysis of Maltulose.—The sugar was hydrolysed with 0·1N-sulphuric acid at 100° overnight. The solution was neutralised by shaking it with Amberlite resin IR-4B, filtered, and concentrated to a syrup, chromatographic analysis of which (solvents *a*, *b*, and *c*) indicated the presence of glucose and fructose. These were separated on sheets of filter paper (solvent *c*). The glucose was characterised as the phenylosazone, m. p. and mixed m. p. 205°, identical with D-glucosazone, and fructose as its 2 : 3-4 : 5-di*iso*propylidene derivative, m. p. and mixed m. p. 93°, $[\alpha]_D^{19}$ −32° (*c*, 0·62 in H_2O).

We thank Professor S. Peat, F.R.S., for the gift of a specimen of maltulose. One of us (E. L. R.) thanks the New Zealand Defence Science authorities for an award.

THE UNIVERSITY, BRISTOL. [*Received, March 17th,* 1953.]

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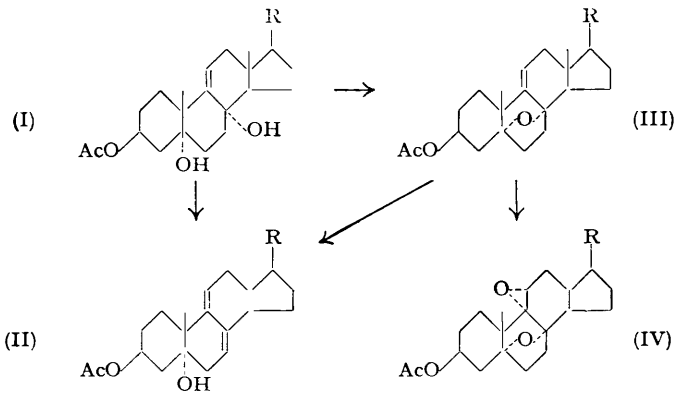
409. *Studies in the Steroid Group. Part LIX.* Preparation and Reactions of 5α : 8α-Epoxy-Δ⁹⁽¹¹⁾-steroids.*

By R. B. CLAYTON, A. CRAWSHAW, H. B. HENBEST, E. R. H. JONES, (MISS) B. J. LOVELL, and GEOFFREY W. WOOD.

5α : 8α-Dihydroxy-Δ⁹⁽¹¹⁾-steroids, prepared by reduction of 9(11)-dehydroergosterol epidioxide, are converted by acetic acid into 5α : 8α-epoxy-Δ⁹⁽¹¹⁾-compounds. Some reactions of this new class of steroid epoxides are described.

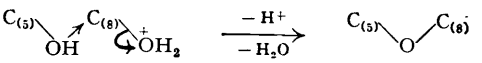
ONE of the aims in preparing 5α : 8α-dihydroxy-Δ⁹⁽¹¹⁾-steroids (I) (by reduction of dehydroergosterol epidioxide; cf. Part LVI, *J.*, 1952, 4883) was to find out whether rearrangements of the allylic 8-hydroxy-Δ⁹⁽¹¹⁾-system to give 11-substituted Δ⁸⁽⁹⁾ compounds could be effected (cf. the rearrangement of 5-hydroxy-Δ⁶- to 7-halogeno-Δ⁵-steroids, Henbest and Jones, *J.*, 1948, 1792). In the present instances, such rearrangements have not been accomplished because under most isomerisation conditions these 5 : 8-dihydroxy-Δ⁹⁽¹¹⁾-compounds were dehydrated to 7 : 9-dienes (II). This dehydration could be carried out quantitatively with dilute mineral acids (Part LVI).



Treatment of these 5 : 8-diols with organic acids, such as acetic acid, also resulted in the loss of the elements of water, but the products obtained (in good yield) were 5α : 8α-epoxides (III). The new compounds were characterised, first, by their relative ease of

* Part LVIII, *J.*, 1952, 4894.

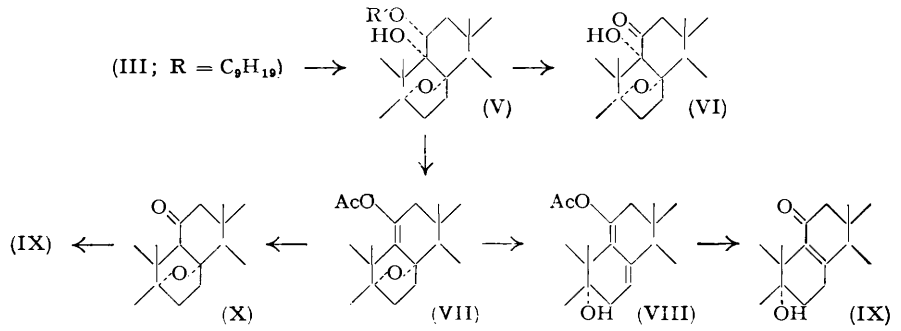
elution from alumina, their lack of characteristic absorption in the ultra-violet above 2200 Å, and the ease with which they were converted by traces of mineral acid into the isomeric 5-hydroxy-7 : 9-dienes (II). The formation of these epoxides parallels the formation of 1 : 4-cineole from 1 : 4-dihydroxy-*p*-menthane (cf. Wallach, *Annalen*, 1912, **392**, 62), and mechanistically may be represented thus :



The configuration of the epoxide bridge must be α in view of the formation from 5α : 8α-diols. Models show that ring B is most likely to adopt a boat conformation in compounds with the stereochemistry of these 5 : 8-diols. In this conformation, the 5α- and the 8α-hydroxyl group are close to each other, and thus favourably disposed for intramolecular dehydration (the formation of these epoxides is discussed further in the following paper).

The reactivity towards oxidising agents of the 9 : 11-ethylenic bond in these 5 : 8-epoxy-compounds was much greater than in the corresponding steroids with a 5 : 8-epidioxy-linking (cf. Part LVIII, *J.*, 1952, 4894). For instance, (III; R = C_9H_{19}), with potassium permanganate in acetic acid or with organic peracids, afforded good yields of the diepoxide (IV; R = C_9H_{19}), whereas the reaction between the 5 : 8-epidioxy-compounds and organic peracids was very slow, and permanganate largely attacked the 12-position. With limited amounts of these oxidising agents and the $\Delta^{9:22}$-5 : 8-epoxide (III; R = C_9H_{17}), some preferential oxidation of the $\Delta^{9(11)}$-bond took place and moderate yields of (IV; R = C_9H_{17}) could be obtained. Permanganate oxidation of (III; R = C_9H_{17}) resulted also in partial degradation of the side chain, yielding the diepoxy-acid (IV; R = CHMe·CO_2H), and in some preferential attack at the Δ^{22}-bond, for methyl 3β-acetoxy-5α-hydroxybisnorchola-7 : 9-dienate could be isolated after treatment of the reaction product with dilute mineral acid and then diazomethane, indicating the presence in the total product of (III; R = CHMe·CO_2H).

Perhaps the greatest difference in reactivity of the $\Delta^{9(11)}$-bond in the 5 : 8-epoxy- and -epidioxy-compounds was towards osmium tetroxide, for whereas the latter class did not react, the former, exemplified by (III; R = C_9H_{19}), gave an addition complex and thence the 9α : 11α-diol (V; R′ = H), the configuration being indicated by the ready formation of an 11-acetate (V; R′ = Ac). Chromic acid oxidised the 9 : 11-diol to the ketol (VI), but attempts to replace the 9-hydroxyl group by hydrogen *via* halogeno-compounds by the methods used by Heymann and Fieser (*J. Amer. Chem. Soc.*, 1951, **73**, 5254) for a similar ketol lacking the oxide bridge were unsuccessful; the 9-hydroxyl group was very unreactive, probably for steric reasons.

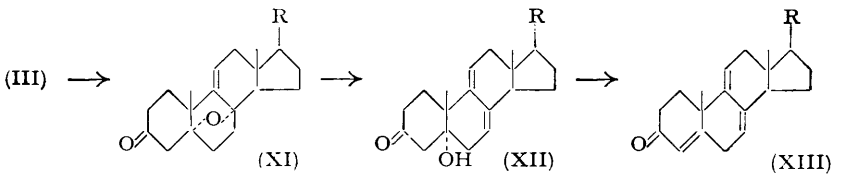


Attempted dehydration of the diol (V; R′ = H) with thionyl chloride in pyridine gave the 9 : 11-sulphite ester, but treatment of the 11-acetoxy-9-hydroxy-compound (V; R′ = Ac) with thionyl chloride in pyridine resulted in ready *trans*-elimination of the elements of water (with ring B necessarily in the boat and ring C in the chair form the 9α-hydroxyl group and the 11β-hydrogen atom are both polar and coplanar with $C_{(9)}$ and

$C_{(11)}$), with the formation of the enol acetate (VII). This was readily isomerised by dilute mineral acid to the 5-hydroxy-7 : 9-diene (VIII) ($\lambda_{max.}$ 2450 Å), although this was not obtained crystalline. Dilute alkaline hydrolysis of the doubly unsaturated enol acetate (VIII) or the epoxy-enol acetate (VII) gave a solution with $\lambda_{max.}$ 2540 Å, corresponding to an 11-keto-$\Delta^{8(9)}$-structure (IX), the intensity of absorption indicating the presence of about 70% of the conjugated ketone. The preparation by other routes of compounds with structure (IX) will be dealt with in a separate paper. The formation of such a conjugated ketone from (VII) on treatment with alkali clearly proceeds *via* the epoxy-ketone (X); the isomerisation of this to (IX) is analogous to the rearrangement of 7-keto-9α : 11α-epoxides to 11α-hydroxy-7-keto-$\Delta^{8(9)}$-steroids (cf. Stork, Romo, Rosenkranz, and Djerassi, *ibid.*, p. 3546).

Reduction of the 5 : 8-oxide system was also studied in view of the possibility of preparing 5-hydroxy-$\Delta^{9(11)}$-compounds. No reaction took place with lithium aluminium hydride until the temperature was raised to the b. p. of dibutyl ether; a mixture was then obtained (some diene, probably 7 : 9, was detected spectroscopically) in which the 5-hydroxy-$\Delta^{8(9)}$ (and possibly the -Δ^{7})-compound was probably present, for treatment with hydrogen–platinum–acetic acid gave 3β-acetoxyergost-8(14)-en-5α-ol. Catalytic hydrogenation was likewise difficult to achieve but using a relatively large amount of Adams catalyst in acetic acid caused uptake of one mol., 3β-acetoxyergost-8(14)-en-5α-ol being isolated; this was probably formed from the 5-hydroxy-7 : 9-diene produced by isomerisation of the epoxide.

Oppenauer oxidation of 3-hydroxy-5 : 8-epoxides yielded ketones (XI), which were fairly stable towards alkali, in contrast to the 7-keto-9 : 11-epoxides and 11-keto-5 : 8-epoxide discussed above. As expected, these ketones were readily isomerised to 7 : 9-dienes (XII) with traces of mineral acid. Dehydration of (XII) was best effected with the weak alkaline reagent, aluminium *tert.*-butoxide, which afforded, when R = C_9H_{17}, the same ketone (XIII) as was obtained by Oppenauer oxidation of 9 : 11-dehydroergosterol.



Experimental

In this and the following paper m. p.s were determined on a Kofler block and are corrected. Optical rotations were determined with chloroform solutions in a 1-dm. semi-micro tube at room temperature (18—25°). P. Spence (Grade H) alumina was used for chromatography; " deactivated alumina " signifies that it had been treated with 5% or 10% acetic acid as described by Farrar, Hamlet, Henbest, and Jones (*J.*, 1952, 2657).

3β-*Acetoxy*-5α : 8α-*epoxyergosta*-9 : 22-*diene* (III; R = C_9H_{17}).—A solution of 3β-acetoxyergosta-9 : 22-diene-5α : 8α-diol (8 g.) in acetone (180 c.c.) and acetic acid (10 c.c.) was heated under reflux for 1 hr. The solvents were then removed under reduced pressure and the residue was introduced in benzene on to a column of alumina (200 g.). Elution with benzene (600 c.c.) gave the 5 : 8-*epoxide* (6 g.), crystallising from methanol as needles, m. p. 115—117°, $[\alpha]_D$ +31° (*c*, 1·15) (Found : C, 79·4; H, 10·3. $C_{30}H_{46}O_3$ requires C, 79·25; H, 10·2%). Elution with ether–methanol (3 : 1) afforded, after crystallisation from acetone, 3β-acetoxyergosta-7 : 9 : 22-triene-5α-ol (1·6 g.) as large plates, m. p. 213—216°, $[\alpha]_D$ +48° (*c*, 0·84).

Hydrolysis (5% methanolic potassium hydroxide) of the epoxy-acetate afforded 5α : 8α-*epoxyergosta*-9 : 22-*dien*-3β-*ol*, crystallising from methanol as laths, m. p. 131—132°, $[\alpha]_D$ +26° (*c*, 0·84) (Found : C, 81·65; H, 10·7. $C_{28}H_{44}O_2$ requires C, 81·5; H, 10·75%).

3β-*Acetoxy*-5α : 8α-*epoxyergost*-9-*ene* (III; R = C_9H_{19}).—This was prepared (in similar yield) as described for the Δ^{22}-compound. The acetate crystallised from methanol as blunt needles, m. p. 106—108°, $[\alpha]_D$ +62° (*c*, 1·2) (Found : C, 78·9; H, 10·9. $C_{30}H_{48}O_3$ requires C, 78·85; H, 10·6%). Alkaline hydrolysis gave 5α : 8α-*epoxyergost*-9-*en*-3β-*ol*, m. p. 102—106°, $[\alpha]_D$ +55° (*c*, 0·95) (after crystallisation from methanol) (Found : C, 81·1; H, 11·25. $C_{28}H_{46}O_2$ requires C, 81·1; H, 11·2%).

Acidic Isomerisation of 5α : 8α-*Epoxy*-$\Delta^{9(11)}$-*steroids*.—(*a*) 5α : 8α-Epoxyergost-9-en-3β-ol (70 mg.) was dissolved in hot methanol and a trace of concentrated hydrochloric acid was added. After 3 min. a dense precipitate of glistening plates was produced. After cooling to 20°, the precipitated ergosta-7 : 9-diene-3β : 5α-diol (60 mg.; m. p. 211—220°) was recrystallised from acetone, giving a product with m. p. and mixed m. p. with an authentic sample 214—220°, $[\alpha]_D$ +44° (*c*, 1·0). Light absorption : Max. 2420 A; ε = 17,000.

(*b*) 3β-Acetoxy-5α : 8α-epoxyergost-9-ene (150 mg.) in hot methanol (3 c.c.) was treated with a trace of concentrated hydrochloric acid. A precipitate separated almost immediately. Cooling the mixture gave 3β-acetoxyergosta-7 : 9-dien-5α-ol (120 mg.), m. p. 195—202°. Recrystallisation from acetone gave material (100 mg.) of m. p. and mixed m. p. with an authentic sample 209—213°, $[\alpha]_D$ +60° (*c*, 1·0). Light absorption : Max. 2420 Å; ε = 17,300.

3β-*Acetoxy*-5α : 8α-9α : 11α-*diepoxyergostane* (IV; R = C_9H_{19}).—(*a*) 3β-Acetoxy-5α : 8α-epoxyergost-9-ene (1 g.) in dry chloroform (2 c.c.) was treated with chloroform (15 c.c.) containing 2·5 mols. of perbenzoic acid. The solution was kept at 20° for 3 days, whereafter the steroid was isolated with chloroform in the usual way. One crystallisation from methanol gave a product (0·78 g.), m. p. 145—150°; a second crystallisation from methanol afforded the *diepoxide* with m. p. 146—150·5°, $[\alpha]_D$ +52° (*c*, 0·93) (Found : C, 76·0; H, 10·1. $C_{30}H_{48}O_4$ requires C, 76·2; H, 10·25%). Absence of appreciable absorption at 2050—2200 and 2900 Å indicated the absence of olefinic and carbonyl groups (absence of the latter was confirmed by the infra-red spectrum).

(*b*) A solution of potassium permanganate (130 mg.) in the minimum amount of acetic acid–water (1 : 1) was added to 3β-acetoxy-5α : 8α-epoxyergost-9-ene (300 mg.) in acetic acid (10 c.c.). The mixture was kept at 20° for 90 min., the steroid being then isolated with ether. Crystallisation from methanol gave the diepoxide (170 mg.), m. p. and mixed m. p. 147—149·5°, $[\alpha]_D$ +54° (*c*, 0·92).

(*c*) A mixture of 3β-acetoxy-5α : 8α-epoxyergost-9-ene (350 mg.) in dioxan (7·5 c.c.) and chloroform (5 c.c.), formic acid (1·5 c.c.), and 100-vol. hydrogen peroxide (1·5 c.c.) was kept at 20° for 60 hr. Isolation with ether and crystallisation from methanol afforded the diepoxide, m. p. 143—144·5°, $[\alpha]_D$ +58° (*c*, 1·0).

3β-*Acetoxy*-5α : 8α-9α : 11α-*diepoxyergost*-22-*ene* (IV; R = C_9H_{17}).—A solution of permonophthalic acid (1 mol.) in ether (25 c.c.) was added to a solution of 3β-acetoxy-5α : 8α-epoxyergosta-9 : 22-diene (3 g.) in ether (25 c.c.). The mixture was kept at 0° for 24 hr. and then at 25° for 48 hr., then diluted with ether and washed successively with sodium carbonate and ferrous sulphate solutions, dried (Na_2SO_4), and evaporated. Concentrated hydrochloric acid (4 drops) was added to a solution of this product in hot methanol. The solution was allowed to cool to 25° and the steroid was isolated with ether. The resulting product in benzene was introduced on to alumina (300 g.). Elution with benzene (600 c.c.) afforded the *diepoxide* (940 mg.) which crystallised from methanol as large needles, m. p. 157·5—159°, $[\alpha]_D$ +21° (*c*, 1·72) (Found : C, 76·5; H, 9·85. $C_{30}H_{46}O_4$ requires C, 76·6; H, 9·9%). Elution with ether–methanol (3 : 1) gave, after recrystallisation from acetone, 3β-acetoxyergosta-7 : 9 : 22-trien-5α-ol, m. p. 214—217°, $[\alpha]_D$ +50° (*c*, 0·83).

Alkaline hydrolysis of this diepoxide yielded 5α : 8α-9α : 11α-*diepoxyergost*-22-*en*-3β-*ol*, crystallising from methanol as plates, m. p. 186—188°, $[\alpha]_D$ +14° (*c*, 1·03) (Found : C, 78·3; H, 10·35. $C_{28}H_{44}O_3$ requires C, 78·45; H, 10·35%).

Reaction of 3β-*Acetoxy*-5α : 8α-*epoxyergosta*-9 : 22-*diene with Potassium Permanganate*.—(*a*) Potassium permanganate (490 mg.) in acetic acid (12 c.c.) and water (2 c.c.) was added dropwise to a solution of the epoxy-diene (600 mg.) in acetic acid (8 c.c.) during 5 min. After being kept at 20° for 1 hr. the mixture was poured into water, and the steroid isolated with ether. The ethereal solution was washed with 2% potassium hydroxide solution (see below), dried, and evaporated. The residue (470 mg.) after seven recrystallisations from methanol afforded almost pure 3β-acetoxy-5α : 8α-9α : 11α-diepoxyergost-22-ene (80 mg.) as needles, m. p. 151—153·5°, $[\alpha]_D$ +24°; mixed m. p. with an authentic sample (see above) 152—158°. Acidification of the alkali extract gave (by ether-extraction) some gummy acid (80 mg.), which was treated with diazomethane and then with 1 drop of hydrochloric acid in methanol, to yield methyl 3β-acetoxy-5α-hydroxybisnorchola-7 : 9-dienoate as plates, m. p. and mixed m. p. (cf. Part LVII, *J.*, 1952, 4890) 189—196°, $[\alpha]_D$ +73° (*c*, 0·53) (Found : C, 71·85; H, 9·05. Calc. for $C_{25}H_{36}O_5$: C, 72·1; H, 8·7%).

(*b*) Potassium permanganate (12 g.) in water (100 c.c.) and acetic acid (400 c.c.) was added with gentle swirling to the epoxy-diene (15 g.) in acetic acid (200 c.c.), with water cooling, and the solution was then kept at 20° for 40 min. The steroid was isolated with ether, the ethereal

solution then being extracted with 10% sodium carbonate solution. Acidification and ether-extraction afforded a crystalline acid (5 g.). Recrystallisation of a small amount of this from dioxan–*iso*propyl ether (1 : 1) gave 3β-*acetoxy*-5α : 8α-9α : 11α-*diepoxybisnorcholanic acid* as needles, m. p. 231—237°, $[\alpha]_D$ +42° (*c*, 1·27) (Found : C, 69·05; H, 8·0. $C_{24}H_{34}O_6$ requires C, 68·85; H, 8·2%). Excess of diazomethane in dry ether was added to part of the crude acid (1·35 g.). Removal of the ether gave a solid, which was dissolved in hot methanol, treated with 10 drops of hydrochloric acid, kept for 4 min., and then poured into water and ether. The ethereal extract yielded a solid which was chromatographed on deactivated alumina (150 g.). Elution with benzene (2 l.) gave *methyl* 3β-*acetoxy*-5α : 8α-9α : 11α-*diepoxybisnorcholanate* (770 mg.), long needles (from aqueous methanol), m. p. 158—159·5°, $[\alpha]_D$ +57° (*c*, 1·23). A portion was sublimed *in vacuo* for analysis (Found : C, 69·25; H, 8·35. $C_{25}H_{36}O_6$ requires C, 69·4; H, 8·4%). Further elution with benzene–ether (19 : 1) (2 l.) gave, after crystallisation from methanol, methyl 3β-acetoxy-5α-hydroxybisnorchola-7 : 9-dienoate (600 mg.) as plates, m. p. and mixed m. p. with an authentic sample 189—194°.

3β-*Acetoxy*-5α : 8α-*epoxyergostane*-9α : 11α-*diol* (V; R′ = H).—Solutions of 3β-acetoxy-5α : 8α-epoxyergost-9-ene (1·6 g.) in dry ether (15 c.c.) and of osmium tetroxide (1 g.) in dry ether were mixed, and pyridine (30 drops) was added. After 4 days at 20° the (now reddish-brown) solution was shaken overnight with an aqueous solution (200 c.c.) containing mannitol (20 g.) and potassium hydroxide (2 g.). The colourless ethereal layer was washed, dried, and evaporated, to give a pale brown solid (1·6 g.). This was chromatographed on alumina (100 g.), the fraction (1·1 g.) eluted with benzene–ether (1 : 1) being crystallised from methanol, to give the 9α : 11α-*diol* as fine needles, m. p. 192·5—194°, $[\alpha]_D$ +68° (*c*, 0·63) (Found : C, 73·5; H, 10·15. $C_{30}H_{50}O_5$ requires C, 73·45; H, 10·25%).

Attempted dehydration of this diol (110 mg.) with thionyl chloride (0·2 c.c.) in pyridine (3 c.c.) at 20° for 45 min., the steroid being isolated with ether, gave after two crystallisations from methanol the *sulphite* of the 9 : 11-diol as fine needles, m. p. 173—174°, $[\alpha]_D$ −28° (*c*, 0·37) (Found : C, 66·95; H, 9·0; S, 5·6. $C_{30}H_{48}O_6S$ requires C, 67·15; H, 9·2; S, 5·95%). Infra-red spectrum (in Nujol) : peaks at 1720 and 1245 (acetate) and 1215 cm.$^{-1}$ (sulphite; cf. Adams, Shafer, and Braun, *J. Amer. Chem. Soc.*, 1952, **74**, 5612).

3β : 11α-*Diacetoxy*-5α : 8α-*epoxyergostan*-9α-*ol* (V; R′ = Ac) *and* 3β : 11α-*Diacetoxy*-5α : 8α-*epoxyergost*-9-*ene* (VII).—A solution of the above 9 : 11-diol (150 mg.) in acetic anhydride (1·5 c.c.) and pyridine (3 c.c.) was heated at 100° for 8 hr. The product was isolated with ether; crystallisation from methanol yielded the 3 : 11-*diacetate*, m. p. 200—200·5°, $[\alpha]_D$ +64° (*c*, 0·71) (Found : C, 71·85; H, 9·85. $C_{32}H_{52}O_6$ requires C, 72·15; H, 9·85%).

Thionyl chloride (0·7 c.c.) was added to a solution of the diacetate (540 mg.) in pyridine (8 c.c.), and the mixture was then kept at 20° for 30 min. The steroid was isolated with ether and purified by chromatography on deactivated alumina (45 g.), elution with light petroleum–benzene (1 : 1) (600 c.c.) giving a solid (290 mg.), which on crystallisation from aqueous methanol afforded 3β : 11α-*diacetoxy*-5α : 8α-*epoxyergost*-9-*ene* as small needles, m. p. 149—152°, $[\alpha]_D$ +100° (*c*, 0·61) (Found : C, 74·95; H, 9·9. $C_{32}H_{50}O_5$ requires C, 74·65; H, 9·8%). Infra-red spectrum (in CCl_4) : peaks at 1750 and 1218 (enol acetate), 1730 and 1240 (3-acetate).

A solution of the enol-acetate (40 mg.) in methanol (15 c.c.) containing 15 drops of concentrated hydrochloric acid was kept at 20°. After 7 hr. the intensity at the absorption maximum (2450 Å) had become stationary (11,600), indicating the presence of about 70% of 7 : 9-diene (VIII). This compound was not obtained solid, but treatment of the product with 5% potassium hydroxide in methanol gave a solution with $\lambda_{max.}$ 2550 Å (ε = 7600). Similar alkaline treatment of 3β : 11α-diacetoxy-5α : 8α-epoxyergost-9-ene afforded a solution with $\lambda_{max.}$ 2530 Å (ε = 7200), the absorption in both cases corresponding to the presence of a 5α-hydroxy-11-keto-$\Delta^{8(9)}$-steroid (IX).

3β-*Acetoxy*-5α : 8α-*epoxy*-9α-*hydroxyergostan*-11-*one* (VI).—3β-Acetoxy-5α : 8α-epoxyergostane-9α : 11α-diol (110 mg.) in acetic acid (10 c.c.) was treated dropwise at 20° during 30 min. with chromic acid (30 mg.) in 70% acetic acid (3 c.c.), the mixture then being kept at 20° overnight. Excess of oxidising agent was reduced with methanol (2 c.c.), and the steroid isolated with ether. Crystallisation from methanol gave a good yield of the 11-*ketone* (VI), m. p. 204—206°, $[\alpha]_D$ +164° (*c*, 0·53) (Found : C, 73·8; H, 10·2. $C_{30}H_{48}O_5$ requires C, 73·75; H, 9·9%). Infra-red spectrum (in Nujol) : peaks at 3460 (hydroxyl), 1730 and 1250 (acetate), and 1695 cm.$^{-1}$ (11-ketone).

3β-*Acetoxyergost*-8(14)-*en*-5α-*ol from* (III; R = C_9H_{19}).—A solution of the epoxide (470 mg.) in acetic acid (20 c.c.) was shaken with Adams catalyst (150 mg.) and hydrogen. Uptake ceased when 1 mol. had been absorbed (1½ hr.). Filtration and removal of the solvent under

reduced pressure gave solid which yielded rods (220 mg.), m. p. 148—161°, from methanol. Further crystallisation afforded the pure $\Delta^{8(14)}$-compound, m. p. and mixed m. p. (sample prepared as described in Part LVI), 161—164°, $[\alpha]_D$ +3·5° (*c*, 1·1).

5α : 8α-*Epoxyergost*-9-*en*-3-*one* (XI; R = C_9H_{19}).—5α : 8α-Epoxyergost-9-en-3β-ol (750 mg.) was heated for 4 hr. under reflux with acetone (15 c.c.), and a 25% solution of aluminium *tert.*-butoxide in toluene (75 c.c.). The cooled mixture was stirred thoroughly with cold water, and the steroid was extracted with ether. Mesityl oxide was removed by evaporation with xylene under reduced pressure, and the product was chromatographed on deactivated alumina (70 g.). Elution with light petroleum–benzene (2 : 1) afforded a crystalline fraction (300 mg.), m. p. 163—168°, which gave the *ketone* as plates (from acetone), m. p. 165—167·5°, $[\alpha]_D$ +122° (*c*, 0·7) (Found : C, 81·8; H, 10·95. $C_{28}H_{44}O_2$ requires C, 81·5; H, 10·75%).

5α : 8α-*Epoxyergost*-9 : 22-*dien*-3-*one* (XI; R = C_9H_{17}).—This was prepared by Oppenauer oxidation of the 3β-sterol as described in the previous experiment. The *ketone* crystallised from methanol as needles, m. p. 147—150°, $[\alpha]_D$ +182° (*c*, 1·0) (Found : C, 81·9; H. 10·3. $C_{28}H_{42}O_2$ requires C, 81·9; H, 10·3%).

A yellow derivative was obtained on treating the ketone with 2 : 4-dinitrophenylhydrazine at 15°. It was filtered off rapidly and recrystallised twice from ethanol, to give small yellow needles melting over a wide range (190—215°), at the same time undergoing conversion into a dark red derivative. Light absorption of the yellow derivative (in chloroform) : Max. 3700 Å; ε = 26,000 (cf. cholestanone 2 : 4-dinitrophenylhydrazone : Max. 3700 Å; ε = 24,500).

5α-*Hydroxyergosta*-7 : 9 : 22-*trien*-3-*one* (XII; R = C_9H_{17}).—The foregoing ketone (100 mg.), dissolved in ethanol (5 c.c.), was treated with a drop of concentrated hydrochloric acid, giving an immediate precipitate. Adddition of water gave more product; crystallisation of the total product from ethyl acetate gave the *hydroxy-ketone* as plates, m. p. 225—230°, $[\alpha]_D$ +76° (*c*, 0·5) (Found : C, 81·75; H, 10·25. $C_{28}H_{42}O_2$ requires C, 81·9; H, 10·3%). Light absorption : Max. 2440 Å; ε = 14,000.

This hydroxy-ketone (200 mg.) was dehydrated by a 25% solution of aluminium *tert.*-butoxide in toluene (20 c.c.) at 100° for 10 min. The product was isolated with ether and chromatographed on deactivated alumina (10 g.). Benzene–light petroleum (1 : 4) eluted a yellow gum (150 mg.) which crystallised in contact with acetone, giving a yellow solid, m. p. 110—130°. Several recrystallisations from aqueous acetone gave ergosta-4 : 7 : 9 : 22-tetraen-3-one (XIII) as plates, m. p. 141—145°, $[\alpha]_D$ +176° (*c*, 0·5), which on admixture with a sample, m. p. 140—145°, $[\alpha]_D$ +178°, prepared by Oppenauer oxidation of dehydroergosterol according to Heilbron, Kennedy, Spring, and Swain (*J.*, 1938, 869), gave no m. p. depression.

Dehydration of the hydroxy-ketone with sodium hydroxide or methoxide in methanol gave gums [owing to the instability of (XIII) towards strong alkali], and sublimation *in vacuo* afforded unchanged hydroxy-ketone.

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